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Sources and Their Preliminary Evaluation as Plasticizers*

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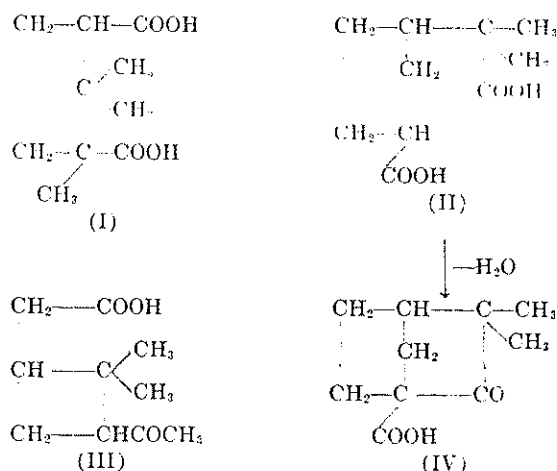
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ONE of the objectives of Army Quartermaster research is increased knowledge leading to the improvement of specific end products, such as plastic materials. The migration of plasticizers—the blooming or exudation of the flexibilizing agent—is a frequent cause of the deterioration of the plastics. In studying this phenomenon it was deemed desirable to synthesize a variety of plasticizing compounds having the general characteristics of compatibility with high polymers, low vapor pressures, high polarity, and low freezing points.

The field of terpene chemistry was particularly attractive for the exploration of new plasticizers because (1) a homologous series of compounds could be readily prepared by well-investigated procedures, (2) terpenes, as a rule, are active solvents for organic high polymers, and (3) sufficient information was available to indicate that the compounds have other desirable properties as plasticizers, namely, fungistatic activity.

Other than camphor, slight attention has hitherto been paid to the terpene field in the search for new plasticizers. It is of interest to note that the diethyl- and the di-n-butyl esters of camphoric acid were introduced as commercial plasticizers in Germany during World War II apparently because no other flexibilizing agents were available for imparting to cellulose acetate those properties which are necessary in photographic and x-ray films.

Inasmuch as the work reported herein is preliminary in nature, the testing of the plasticizing action of the compounds was confined to a determination of com-



patibilities with selected high polymers, flexibilizing properties at low temperature and fungistatic activity.

EXPERIMENTAL

Terpene Carboxylic Acids

The d-camphoric acid was obtained from a commercial source and was of high purity. The camphenic acid was prepared (1) by oxidizing camphene

Table I. Properties of Terpene Carboxylic Acids

Terpene carboxylic acid	M.p. ^a	[Alpha] _D ²⁰	Calcd.	Neutr. equiv. Found	Origin
d-Camphoric acid, C ₁₀ H ₁₆ O ₄	187°	+47.1	200.23	200.4	Commercial product
Camphenic acid, C ₁₀ H ₁₆ O ₄	136.5-138°	...	200.23	201.2	Oxidation of com. camphene
Camphenonic acid, C ₁₀ H ₁₄ O ₃	133-134°	...	182.00	182.0	Camphenic acid
Nopinonic acid, C ₁₀ H ₁₆ O ₃	128°	...	184.20	181.2	Beta-pinene from sulphate turpentine
dl-Pinonic acid, C ₁₀ H ₁₆ O ₃	102-104°	-1.09°	184.20	184.5	alpha-pinene (wood turpentine)
"Liquid pinonic acid"	Liquid	+15.07°	...	206.8	alpha-pinene (wood turpentine)
dl-Pinonic acid, C ₁₀ H ₁₆ O ₃	99.5-101.5°	...	184.20	184.0	crude sulphate turpentine
"Liquid pinonic acid"	Liquid	+23.5°	...	252.6	

^a All melting points reported in this paper are uncorrected.

The compounds selected for investigation included certain esters of d-camphoric acid (I), its asymmetric isomer, camphenic acid (II), pinonic acid (III) and camphenonic acid (IV):

The possibility of using crude mixtures of terpene carboxylic acids, from an economy viewpoint, for starting materials was explored, and the esters thus prepared were compared with authentic compounds. Crude sulphate turpentine was studied as a convenient raw material for the preparation of pinonic acid.

Table II. Comparison of Pinonic Acids from Alpha-Pinene and Crude Sulphate Turpentine

Pinonic acid	From alpha-pinene	From crude sulphate turpentine
"Crude pinonic acid"	50% yield	45% yield
dl-pinonic acid	25% yield	25% yield
melting point	102-104°C.	99.5-105.0°C.
[alpha] _D ²⁰	-1.09°C.	...
"Liquid pinonic acid"	25% yield	18% yield
[alpha] _D ²⁰	+15.07°C.	+23.5°C.
d ₄ ²⁰	1.07667	1.07289
n _D ²⁰	1.4682	1.4742
Neutr. equiv.	206.8	252.6

^a Higher yields may be obtained by using the procedure of Dupont (*Ann. chim.* 1923 (ix) 19: 186).

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Table III. Properties of Esters from Pure Terpene Carboxylic Acids

Ester	Boiling point °C., pressure in microns	Analysis calculated C, %	H, %	Analysis found ^b C, %	H, %	d ₄ ²⁰	n _D ²⁰	Molecular Calcd.	Refraction Found
d-Camphoric-di-n-hexyl-, C ₂₂ H ₄₀ O ₄ ^a	159-161.5/65	71.69	10.94	70.60	10.37	0.96468	1.4597	104.47	104.46
Camphenic-di-n-hexyl-, C ₂₂ H ₄₀ O ₄	156-157.5/165	71.69	10.94	71.88	10.98	0.9573	1.4541	104.47	104.51
Camphenonic-n-hexyl-, C ₁₆ H ₂₆ O ₃	151-151.5/250	72.14	9.83	71.70	9.43	1.00154	1.4649	73.40	73.40
dl-Pinonic-n-hexyl-, C ₁₆ H ₂₆ O ₃	140-141.5/55-60	71.59	10.51	71.86	10.16	0.95417	1.4561	75.43	76.47

^a [Alpha]_D + 18.95°.^b Analyses by S. Sadler & Sons, Philadelphia, Pa.

with alkaline potassium permanganate solution. The same procedure (2) was employed for obtaining nopinic acid from beta-pinene. Camphenonic acid was made by refluxing camphenic acid with acetic anhydride (3). The directions of Bayer et al. (4) were followed for preparing pinonic acid from alpha-pinene. The dl-pinonic acid separates as a solid from the crude vacuum-distilled acid mixture, the liquid part being a mixture

esters involved refluxing the acid and alcohol in the presence of 0.02% of benzene sulphonic acid and a water-carrying-over reagent, xylene or toluene. After the esterification was complete the ester was purified by fractional distillation in a vacuum. Table III shows the properties of the esters obtained from pure acids and Table IV similar data for esters prepared from "crude" and "liquid" pinonic acid.

Table IV. Properties of Esters from Crude and Liquid Pinonic Acids

Ester	Boiling point °C., pressure in microns	d ₄ ²⁰	
Pinonic-n-hexyl	113-114/260	0.9623	From alpha pinene ("Liquid pinonic" acid)
Pinonic-n-hexyl	138-145/350-375	0.97107	From crude sulphate turpentine ("Liquid pinonic" acid)
Pinonic-cyclohexyl	145/190	1.0246	From crude sulphate turpentine ("Crude pinonic" acid)
Pinonic-benzyl	160-190/200-250	1.0522	From alpha pinene ("Crude pinonic" acid)
Pinonic-benzyl	150-152/180	1.06965	From crude sulphate turpentine ("Crude pinonic" acid)
Pinonic-methyl	75-79/400	1.2638	From alpha pinene ("Crude pinonic" acid)
Pinonic-ethylenemonoethylglycol	120.5-121.5/100-150	...	From alpha pinene ("Crude pinonic" acid)
Pinonic-2-ethylhexylglycol	125-140/125-195	1.03266	From alpha pinene ("Crude pinonic" acid)
Pinonic-acid "terpene alcohol" ^a	118-184/260	1.04315	From alpha pinene ("Crude pinonic" acid)
Dihydrocumic-n-hexyl	129-133/175	0.96028	From nopinic acid (from beta-pinene-sulphate turpentine)

^a The "terpene alcohol" is the poorly defined mixture of glycols and alcohols obtained on oxidation with potassium permanganate in neutral solution according to Delepine, et al., *Ann. chim.* 1943 (iv) 18: 250.

of pinonyl formic, pinic, norpinic, and optically active pinonic acids (5). In this investigation the liquid part is designated as "liquid pinonic acid" and the crude terpene mixture as "crude pinonic acid." Table I records the properties of the acids prepared.

The observation was made that unrefined crude sulphate turpentine can be used with advantage as starting material for producing "crude pinonic acids." The acids are similar in composition to the product obtained from alpha-pinene (Table II). The divergences are of the order to be expected from the use of crude technical raw materials without refining. It should be noted that the mercaptan odor of the crude sulphate turpentine disappears during the oxidation step.

Esters of Terpene Carboxylic Acids

The method employed for the preparation of the

The alcohols employed were commercial products of high purity.

The d-camphoric-di-n-hexyl ester could not be obtained free of d-camphoric anhydride by distillation in a vacuum of the crude n-hexyl ester, regardless of whether the product was prepared by refluxing d-camphoric acid and the alcohol component in the presence of benzene sulphonic acid or obtained by reacting the di-silver salt of d-camphoric acid with n-hexyl iodide. This is in agreement with the previous observation of Brühl (6) that esters of d-camphoric acid are not stable to heat.

Solidification Points of Terpene Carboxy Acid Esters

The determination was carried out in the following manner: A test-tube containing about 2 ml. of ester was cooled in a mixture of dry-ice and ethyl ether and

Table V. Solidification Points of Terpene Carboxy Acid Esters

Test materials	Freezing points, °C.	Remarks
Pinonic methyl ester	-77	Crystalline
Pinonic ethylenemonoethyl glycol ester	-66	Noncrystalline
Pinonic benzyl ester	-52	Noncrystalline
dl-Pinonic n-hexyl ester	-79	Plastic below these temperatures
Pinonic n-hexyl ester (from liquid acid)	-75	Plastic below these temperatures
Camphenic di-n-hexyl ester	-79	Plastic below these temperatures
n-Butyl phthalate	-74	Crystalline
Methyl phthalate	-2	Crystalline
Commercial phthalate No. 1	-44	Nonplastic below these temperatures
Commercial phthalate No. 2	-36	
Commercial phthalate No. 3	-50	

Table VI. Fungicidal Activity of Test Compounds

Compound	Per cent inhibition
d-Camphoric-di-n-hexyl ester	6
Camphenic acid	7
Camphenic di-n-hexyl ester	9
Methyl salicylate	12
Nopinic acid	14
d-Camphoric acid	15
dl-Pinonic acid (from alpha-pinene)	15
Crude pinonic acid (from crude sulphate turpentine)	15
Pinonic ethylenemonoethyl glycol ester	20
Liquid pinonic acid (from alpha-pinene)	20
Pinonic methyl ester	26
Salicylic acid	40
Benzoic acid	42
n-Hexyl benzoate	48
Pinonic n-hexyl ester	50
dl-Pinonic n-hexyl ester	51
Pinonic benzyl ester	54

Table VII.

Ester	Clarity			Shrinkage, %			Flexibility at 80°C.				Flexibility below -50°C.				Origin
	Cellulose triacetate	Cellulose propionate	Polyvinylbutyral	Cellulose acetate	Cellulose triacetate	Cellulose propionate	Polystyrene 1:4 ratio	Polystyrene 1:8 ratio	Polyvinylbutyral	Cellulose acetate	Cellulose triacetate	Cellulose propionate	Polystyrene 1:4 ratio	Polystyrene 1:8 ratio	
d-Camphoric-di-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	Commercial d-camphoric acid
Camphonic-di-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	Commercial camphene
dl-Pinonic-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene
Pinonic-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene "liquid pinonic" acid
Pinonic-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	"Liquid pinonic" acid from crude sulphate turpentine
Pinonic-cyclohexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	"Crude pinonic" acid from crude sulphate turpentine
Pinonic-benzyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	"Crude pinonic" acid from crude sulphate turpentine
Pinonic-benzyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene
Pinonic-methyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene
Pinonic-ethyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene
Pinonic-ethyl-nemomethylglycol-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene
Pinonic-2-ethylhexylglycol-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	alpha-pinene
Dihydrocumin-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	Nopinonic acid from beta-pinene
Camphonic-n-hexyl-	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	Camphonic acid
Pinonic and "terpene alcohol"	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	See Table IV
Commercial phthalyl plasticizer No. 1	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	
Commercial phthalyl plasticizer No. 2	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	
Commercial phthalyl plasticizer No. 3	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	
Blank	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	
n-Butyl sebacate	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	

Legend: C = clear and compatible; F = flexible; NF = nonflexible.
a Cast on mercury.

a glass rod was moved slowly in the liquid. The temperature, at which the glass rod could not be moved due to crystallization or to the viscosity of the liquid, was recorded and designated as the solidification point. In Table V the values obtained for some of the terpene carboxylic acid esters are compared with some phthalic ester plasticizers.

Fungistatic Properties of Terpene Carboxylic Acids and Esters

Some of the terpene derivatives were tested for their fungistatic action. The screening procedure included the incorporation of the test compound into Czapek's agar in a concentration of 250 p.p.m., inoculation with *Aspergillus niger*, (QM 458) and incubation for 96 hours at 85 to 95°F. and 85 to 90% relative humidity. Results were calculated in terms of percentage inhibition based on the average diameter of the test plate colonies compared to the average diameter of the normal untreated controls and controls containing n-hexyl benzoate and methyl salicylate. The results are shown in Table VI.

Esters of Terpene Carboxylic Acids as Plasticizers in Films

Preparation of Films. A stock solution of the resin was made by dissolving 70 grams of the resin in 1000 grams of the solvent by mechanical shaking. To 53.5 grams of this stock solution was added 0.875 grams of plasticizer making the ratio of plasticizer to resin equal to 1:4. Duplicate 25-gram portions of the solution were poured into Petri dishes of 9.5 cm. diameter and the solvent allowed to evaporate over a period of approximately 3 days. The procedure is substantially the same as outlined by Reinhart et al. (7).

Evaluation of Films. Compatibility and clearness were determined by visual observation alone. Per cent shrinkage less than 3% was considered negligible. Flexibility at room temperature (20°C.) was determined by folding a square centimeter of the film on an axis first in one direction and then in the opposite direction. The film is folded again on an axis which is perpendicular to the first axis. Any break in the film by these Schopper folds caused it to be considered nonflexible, and any whitening indicated incompatibility.

To determine the flexibility below -50°C., 1 sq. cm. of the film was placed in a test tube which was immersed in a dry-ice acetone bath. After a period of approximately 5 minutes, the film was tested for flexibility as previously described but with the exception that the film after each folding was kept chilled for about 5 minutes. Table VII records the results obtained.

Infrared Absorption Curves

The dl-pinonic acid and "liquid pinonic acid" from alpha-pinene and crude sulphate

turpentine, and anisic acid were characterized by their infrared absorption curves.

It is of interest that the products derived from crude sulphate turpentine show a characteristic absorption band at 6.2 and 7.9 μ , which is indicative of anisic acid. This acid is the potassium permanganate oxidation product of methylchavicol (4-methoxyallylbenzene), which is a natural constituent of turpentine from slash and long leaf pines as described some years ago by one of us together with Hampton (8).

CONCLUSIONS

The preliminary evaluation of the plasticized films showed that all the esters were compatible with the cellulose esters tested with the exception of the n-hexyl esters of d-camphoric and camphenic acids, which caused blooming in acetate films of 53.2% acetyl content when employed in concentrations less than 1:4 ratio of plasticizer to resin. In polyvinyl butyral films the terpene carboxy esters were as efficient as the commercial phthalate plasticizer used as a blank. The esters, when incorporated in polystyrene films in a 1:3 ratio, showed the same behavior as n-butyl sebacate, but in lower concentrations produced less flexibility than the commercial product.

It was revealed that the n-hexyl esters of dl-pinonic

acid exerted a fungistatic action comparable to esters of benzoic and salicylic acids.

The slight difference in plasticizer behavior between esters of pinonic acid prepared from alpha-pinene and from crude sulphate turpentine is attributed to esters of anisic acid and dihydrocumic acid, an unsaturated aromatic acid, deriving from nopinic acid, which is an oxidation product of beta-pinene. Nopinic acid yields dihydrocumic acid on dehydration because of the unstable hydroxy group in the "I"-position of the pinene nucleus (9).

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